

Thermal Isomerizations of Vinylcyclopropanes to Cyclopentenenes

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ABSTRACT: The thermal isomerization of vinylcyclopropane to cyclopentene was discovered in 1960 and soon recognized as the simplest known example of a [1,3] sigmatropic shift. Experimental observations for the parent rearrangement and for isomerizations shown by substituted systems suggest that diradical transition structures are involved; recent theoretical treatments of the reaction find no minima corresponding to diradical intermediates. The common dichotomy opposing concerted versus diradical and thus necessarily stepwise mechanisms appears inappropriate. The reaction of vinylcyclopropane may involve four energetically concerted paths traversed by different conformational forms of nearly isoenergetic diradical species leading through four isometric diradical transition structures to cyclopentene. © 1998 John Wiley & Sons, Inc. *J Comput Chem* **19**: 222–231, 1998

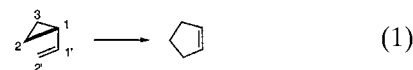
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Introduction

1-Vinyl-2,2-dichlorocyclopropane was found to isomerize to 4,4-dichlorocyclopentene in 1959;¹ the thermal conversions of vinylcyclopropane to cyclopentene and of 1-phenyl-1-vinylcyclopropane to 1-phenylcyclopentene were reported in 1960.^{2–4} Gas phase kinetic studies on the

parent hydrocarbon^{5,6} soon identified the isomerization to cyclopentene as a unimolecular process and the activation parameters found made it seem possible or even likely that relief of ring strain and allylic resonance stabilization of a diradical structure both facilitated cleavage of the cyclopropyl carbon–carbon bond.^{7–12}

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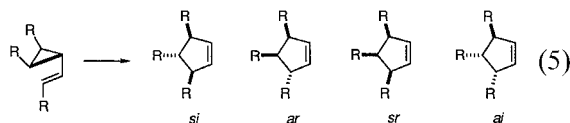


trimethylene diradical intermediate have led to a consensus, or nearly a consensus, which is somewhat more elaborate than the models advanced initially by Hoffmann, Salem, and others.^{32–42} Although some issues related to the dynamic behavior of trimethylenes are today treated differently by different formalisms or calculational approaches,^{43–46} all active participants in this area seem to agree that stereomutations take place through cleavage of a cyclopropyl carbon–carbon bond to give a very short-lived edge-to-edge trimethylene species either through a conrotatory or a disrotatory process; the intermediate may collapse to form a cyclopropane in either a conrotatory or disrotatory fashion, thus permitting formation of either net one-center or two-center epimerization products (diastereomers or enantiomers); and a one-center epimerization may also take place without involvement of an intermediate, by way of an edge-to-face transition structure.

The net result of all these options, and the fact that alternative transition structures are of very similar energies, is that one-center and two-center epimerizations for isotopically labeled cyclopropanes and for substituted cyclopropanes usually take place at very comparable rates. The major energetic barrier for a cyclopropane stereomutation is associated with bond cleavage, and that barrier is nearly insensitive to the stereochemical details of hydrogen dispositions at the terminal methylene units of the trimethylene system.

Conservation of Orbital Symmetry

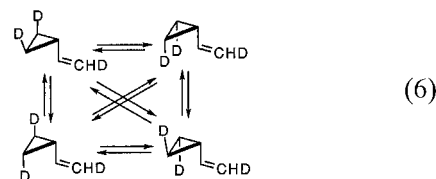
Considerations based on the principle of conservation of orbital symmetry in chemical reactions as formulated in the Woodward–Hoffmann rules led from 1965 on to a wealth of new understandings and much new chemistry.⁴⁷ Inevitably, the rules were applied, most judiciously, to the vinylcyclopropane rearrangement, a prototypical carbon [1,3] sigmatropic rearrangement.^{47, 48} Woodward and Hoffmann recognized that a two-step, nonconcerted path is not thermodynamically unreasonable, yet it was deemed worthwhile to consider the stereochemical consequences of the possible concerted processes for the vinylcyclopropane to cyclopentene change. Two of the four possible paths were, of course, symmetry-allowed, the *suprafacial*, *inversion* and *antarafacial*, *retention* alternatives (*si* and *ar*); the *sr* and *ai* paths were not symmetry allowed:



Interestingly, for the maximally labeled derivative used by Woodward and Hoffmann to illustrate these truths, as shown above, one starting material gave rise to three distinguishable products through the four paths; the *ar* and *ai* paths gave a common product, the racemic *cis*,*trans* isomer. One had to wonder how to determine experimentally all four paths! And, just as interestingly, no predictions as to the true course of the rearrangement were made.

Reaction Stereochemistry

Vinylcyclopropane, like cyclopropane, may suffer thermal stereomutations, and these epimerization reactions may be detected through experiments with deuterium-labeled analogs. Willcott and Cargle demonstrated these degenerate isomerizations in 1967 when they found that the d_3 -labeled vinylcyclopropanes shown interconvert thermally one with another much faster than they isomerize structurally through [1,3] carbon shifts to form cyclopentenenes.^{49, 50}



Thus, cyclopropane stereomutations and the vinylcyclopropane rearrangement are entwined kinetically. Questions regarding reaction stereochemistry for the rearrangement, it was clear, would not be so easy to answer, for stereochemically well-defined starting materials would lose stereochemical integrity much faster than they would give stereoisomeric cyclopentene products. This discouraging reality did not auger well for successful work to establish reaction stereochemistry for the rearrangement.

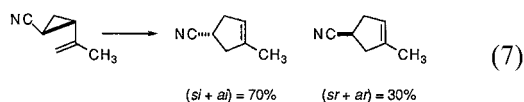
In spite of the apparent difficulties, the quest for mechanistically valuable stereochemical information was not abandoned. It was rather encouraged

when early stereochemical studies on several systems demonstrated that some stereochemical preferences were reflected qualitatively in product mixtures.

Careful studies of thermal automerizations of bicyclo[3.1.0]hex-2-enes by several groups showed that [1,3] shifts occurred with stereochemical preferences and, incidentally, by non-symmetry-allowed paths, without recourse to forcing conditions.⁵¹⁻⁵⁵

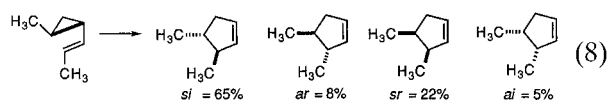
Mazzocchi and Tamburin in 1970 showed that different diastereomers of 1-(*E*-propenyl)-2-ethoxycarbonyl-3-methylcyclopropane gave rise to different mixtures of cyclopentene products as they equilibrated through stereomutations.^{56,57} Neither complete stereorandomization of vinylcyclopropane isomers prior to the rearrangement nor a long-lived, completely stereorandomizing diradical intermediate could account for their observations. Apparently buried somewhere in the kinetic complexity there were stereoselective paths which might be delineated.

Doering and Sachdev followed the thermal epimerizations of enantioenriched 1-cyano-2-isopropenylcyclopropanes and the much slower isomerizations to the two enantiomers of 1-methyl-4-cyanocyclopentene.^{58,59} They were able to deduce the rate constants for [1,3] shifts with retention and inversion at the migrating carbon: the *trans* substrate shown favored inversion, 70:30, whereas *cis*-1-cyano-2-isopropenylcyclopropane showed a 40:60 balance between inversion and retention:

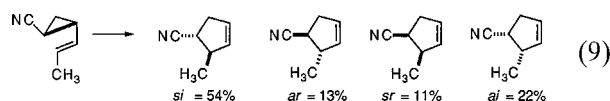


Andrews investigated the thermal chemistry of enantioenriched 1-(*E*-propenyl)-2-*trans*-methylcyclopropane and determined rate constants for racemization, isomerization to acyclic diene, and formation of the four 3,4-dimethylcyclopropanes.⁶⁰ Rate constants for the four stereochemically distinguishable paths were then deduced. The results, displayed in percentage terms relative to all [1,3] shifts, showed that all four paths were utilized, to unequal but not drastically unequal extents. The balance between "allowed" and "forbidden" paths was 73:27. The results were taken to be consistent with four kinetically competitive concerted processes, two allowed and two forbidden; the possi-

ble involvement of a planar π -cyclopropane intermediate was mentioned:



Barsa⁶¹ extended the work on 1-alkenyl-2-cyanocyclopropanes begun by Doering and Sachdev. Enantioenriched samples of the *cis* and *trans* isomers of 1-(*E*-propenyl)-2-cyanocyclopropane of known absolute configuration and enantiomeric excess were prepared, and absolute stereochemical assignments for enantiomerically pure samples of *cis* and *trans* isomers of 3-methyl-4-cyanocyclopentene were secured. The thermal isomerizations of chiral *cis* or *trans* starting materials were then followed, so that both the stereomutations and the [1,3] shifts to give cyclopentenenes could be unraveled. The results for the *trans* substrate are shown:



Overall, the two inversion paths from the *trans* isomer amount to some 76% of all paths, as compared with the 70% figure reported for *trans*-1-isopropenyl-2-cyanocyclopropane⁵⁹ and *trans*-1-(*E*-propenyl)-2-methylcyclopropane.⁶⁰ Both *sr* and *ai* orbital symmetry "forbidden" paths were in evidence.

Other priorities claimed our attention for the next 15 years; finally, we returned to vinylcyclopropane rearrangements prompted in part by additional reports of stereochemical findings.^{62,63} From 1991 to 1996 complete stereochemical information was secured for another six cases of the rearrangement, having in common substituents (deuterium or methyl or phenyl) at 2'-*E* and 2-*trans* positions.⁶⁴⁻⁷¹ The stereochemical results obtained for these systems, including the parent hydrocarbon labeled suitably with deuterium at C2, C3, and C2', depended on the experimental skills of different collaborators. The studies used different kinetic methods and analytical tools and data reduction strategies. The stereochemical findings are remarkably consistent from system to system, in spite of the substantial range of substituents employed. All four possible paths are used, although

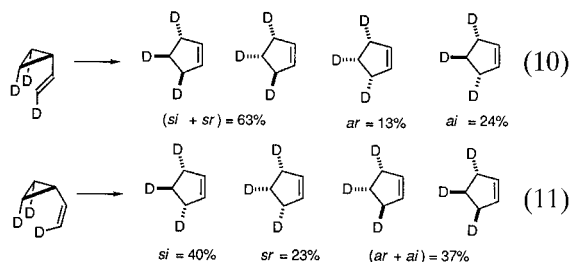
some are used more than others. The *si* product is favored in all cases.

The details of experimental work behind the results summarized above need not be recounted here. But perhaps some comment is in order, in response to a statement made in a recent theoretical study:

Most of the experimental works which aimed to [determine reaction stereochemistry for the vinylcyclopropane rearrangement] were invalidated because parallel processes caused the rapid enantiomerization, or diastereomerization, of species which had been especially designed and synthesized to carry out this type of study.

This judgment is wrong. If one fails to account quantitatively for stereochemical scrambling in a starting material, then of course one cannot interpret product stereochemistry with confidence; but by treating the whole competitive kinetic situation at hand analytically, reliable information on reaction stereochemistry can be gained.

Take, for example, the parent case, adorned with three deuterium labels. As demonstrated first by Willcott and Cargle,^{49,50} rapid stereomutations of this system take place before substantial amounts of 3,4,5-*d*₃-cyclopentene isomers are formed. So, one has to keep track of these stereomutations, calculate time-weighted average relative concentrations of each isomeric form of the reactant over each reaction time, and calculate from the stereochemical character of the product mixture at suitably low conversions (well before the substrate isomers reach equilibration) rate constants for the individual paths. This is an entirely feasible undertaking, and it has been accomplished.⁶⁷ All four stereochemically distinct paths



are utilized to comparable although not equal extents.

Other stereochemical findings for vinylcyclopropanes incorporating a bulky *tert*-butyl group at C1' and having either a *trans* methyl substituent at C2 or *cis* deuterium labels at C2 and C3 have been obtained by Gajewski and co-workers.⁷²⁻⁷⁴

Kinetics and Activation Parameters

The kinetics of the rearrangement of vinylcyclopropane at 325° to 391°C determined in the 1960s in static reactors were consistent with the activation parameters $\log A = 13.5$ – 13.6 and E_a 49.6–49.7 kcal/mol.^{5,6} Similar results were obtained later at 407° to 527°C.⁷⁵ But, recent studies of the interconversion of cyclopentene-3-¹³C with cyclopentene-4-¹³C by way of the intermediate vinylcyclopropane-2-¹³C suggest a slight inconsistency between rate constants extrapolated from the static reactor studies to higher temperatures⁷⁶:

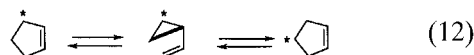


TABLE I.
Stereochemical Paths Utilized in Some Vinylcyclopropane Rearrangements.

R-2 R-2'	R-2'	si (%)	ar (%)	sr (%)	ai (%)
D	D	40	13	23	24
CH ₃	D	55	15	18	13
CH ₃	CH ₃	65	8	22	5
CH ₃	C ₆ H ₅	60	10	19	11
C ₆ D ₅	D	58	8	24	10
C ₆ H ₅	CH ₃	44	20	25	11
C ₆ H ₅	C ₆ H ₅	67	12	17	4

Further work on the isomerization of vinylcyclopropane to cyclopentene using both static reactor and shock tube methods gave first order rate constants over a wide temperature range, 304° to 781°C (577–1054 K) and the activation parameters $\log_{10} (A, \text{s}^{-1}) = 14.3$ and $E_a = 51.7$ kcal/mol.⁷⁷

These recent studies and the heat of formation for vinylcyclopropane allow one to estimate a heat of formation for the transition structure, 82.1 ± 0.6 kcal/mol. A strain-free diradical model for the putative diradical gives $\Delta H_f = 77.5 \pm 0.8$ kcal/mol. The transition structure, then, retains some 4.6 ± 0.9 kcal/mol of ring strain and torsional strain energy.⁷⁷

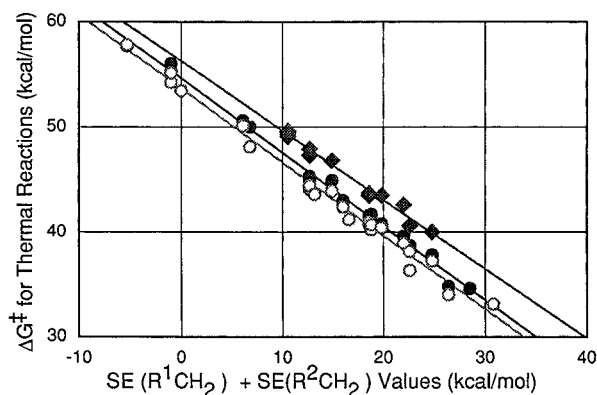


FIGURE 1. Correlations⁷⁸ between ΔG^\ddagger ($k_1 + k_2$) (open circles), ΔG^\ddagger (k_{12}) (solid circles), and ΔG^\ddagger (k_i) (solid diamonds) for *trans*-1-*R*¹,2-*R*²-cyclopropanes and *E*-2'-*R*¹,*trans*-2-*R*²-vinylcyclopropanes with a measure of the radical stabilization capacity of the substituents.

When one compares rates of isomerization of substituted vinylcyclopropanes with rates of stereomutations for substituted cyclopropanes, including vinylcyclopropanes, a common response to the radical stabilizing capacities of substituent groups is apparent. Figure 1 shows linear correlations of ΔG^\ddagger values calculated from reported first-order rate constants for one-center epimerizations ($k_1 + k_2$), for two-center epimerizations (k_{12}), and for isomerizations of vinylcyclopropanes to cyclopentenes (k_i).⁷⁸

All three processes are facilitated by radical stabilizing substituents to a very similar extent. One-center epimerizations [geometrical isomerizations; ($k_1 + k_2$)] are generally favored, slightly, over two-center epimerizations (enantiomerizations; k_{12}); vinylcyclopropane rearrangements (k_i) are slower. The ($k_1 + k_2$) and k_{12} stereomutation processes involve diradical transition states. One may then conclude that the transition structures involved in vinylcyclopropane rearrangements are diradicals or, more fuzzily, diradicaloid in nature, leaving open the possible involvement of diradical intermediates.

Kinetic Isotope Effects

Chickos discovered substantial secondary deuterium kinetic isotope effects for the vinylcyclopropane rearrangement: at 338.5°C, the intermolecular k_H/k_D effects for d_2 -substitution at C2 or at C3, and at C2', are 1.14 ± 0.02 and 1.17 ± 0.02 , respectively.⁷⁹ If the effect at C3 were, say, a mod-

est 5%,³⁷ the effect at the migrating carbon, C2, would be 1.25, or 12% per deuterium; the corresponding product ratio for the cyclopentenes would favor 3,3- d_2 - over 4,4- d_2 -substitution, 54 : 46. Thus, one may infer that there is a large normal isotope effect at the migration origin, C2; at the migration terminus C2' one has a combination of two effects, one for each diastereotopically distinct hydrogen or deuterium.

These two k_H/k_D effects have been determined through kinetic work with *Z*- and *E*-2'- d -vinylcyclopropanes and are, respectively, 1.08 ± 0.05 and 1.15 ± 0.03 at 341°C; for the C2'- d_2 system at this temperature the measured k_H/k_D effect is 1.21 ± 0.03 .⁸⁰ The torsional distortions or hybridization changes at C2' in the transition structure are apparently experienced very differently by the two distinct C2' hydrogens. There has apparently been no theoretical or experimental work to estimate or determine possible diastereotopically distinct k_H/k_D effects at the migrating carbon.

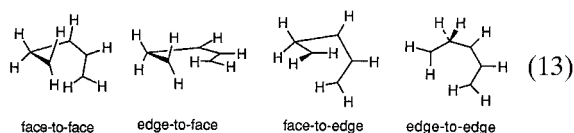
Hypothetical Mechanism

Any postulate of a detailed description for the rearrangement must take into account the conformational options available to a vinylcyclopropane, the thermal behavior of cyclopropanes, the conformations of trimethylene diradicals, what might be expected for a diradical species formed from a vinylcyclopropane, and the relevant experimental observations recounted above.

The conformational situation for vinylcyclopropane is well established through electron diffraction studies^{81–83} and computational work at several levels of theory.^{84,85} There are stable gauche and more stable trans conformations ($\Delta E = 1.2$ kcal/mol), with torsional barriers of 3.1 kcal/mol separating them and of 1.4 kcal/mol between the two equivalent gauche forms. The H—C1—C1'—H torsional angle for the gauche conformer is 56° experimentally⁸² and 62.2° according to *ab initio* calculations.⁸⁵

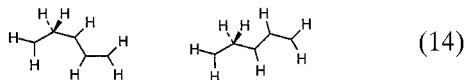
In general, carbon [1,3] shifts in systems such as vinylcyclopropanes,⁸⁶ bicyclo[2.1.1]hex-2-enes,⁸⁷ and bicyclo[3.2.0]hept-2-enes^{88–91} are initiated by carbon-carbon bond cleavage; when the bond is essentially broken torsion changes may become significant. By analogy with cyclopropane, a thermally activated C1—C2 bond cleavage in vinylcyclopropane could provide a face-to-face diradical or, through torsion on the order of 90° about either

the C2—C3 bond or the C1—C3 bond, two different edge-to-face diradicals, or through such torsions about both C2—C3 and C1—C3, the C_s -symmetric edge-to-edge diradical structure. One, several, or all of these diradicals might possibly lie on or very near to a reaction path from vinylcyclopropane to cyclopentene:



These diradicals would be expected to have rotational barriers about C1—C1' and C1'—C2' of about 13 kcal/mol: the C1—C1' barrier would be much higher than in vinylcyclopropane, but the C1'—C2' rotational barrier would be much diminished. Torsional modes at C2' in these diradicals would be expected to be energetically cheap, and slow relative to higher energy modes, such as the C1—C3—C2 bond angle vibration.

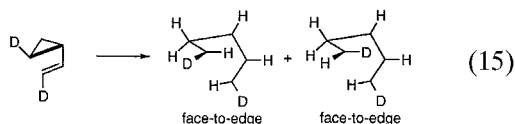
Similar processes could lead to diradicals that could not provide cyclopentenenes due to geometrical limitations but that could progress to give stereomutation products:



The face-to-face trimethylene diradical is a second-order stationary point on the potential energy surface, not a transition structure and not an intermediate; it only leads back to cyclopropane.³⁷ Perhaps with the vinyl substituent, though, a face-to-face diradical would have a sufficiently weakened C1—C2 bond to allow the diradical to distort and accommodate bonding between C2 and C2'.

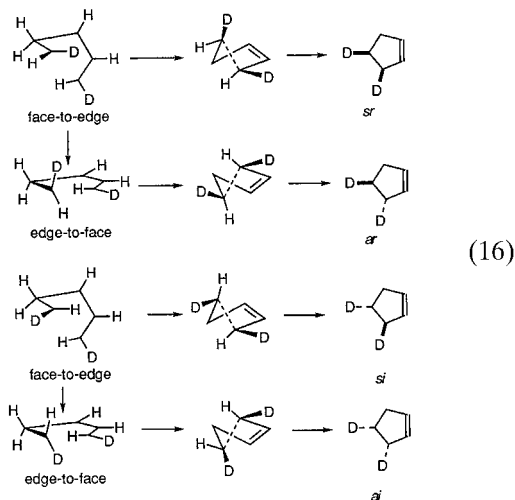
This picture may be elaborated, speculatively, to imagine how stereochemically distinct paths might be traversed. The parent system with the two deuterium labels shown could break the C1—C2 bond through increasing the C1—C3—C2 bond angle and rotating about the C2—C3 bond, in either a counterclockwise or clockwise sense, to approach two distinct face-to-edge diradical structures. Presumably the counterclockwise rotation

would be favored kinetically:



Slight geometrical distortions from each of these face-to-edge structures could give either a transition structure leading to a cyclopentene product or to an edge-to-face diradical which could proceed with some conservation of angular momentum to another transition state and another cyclopentene.

Thus, the four distinct cyclopentenenes might be formed through four separate paths. Further, the four transition structures in the four cases could well be isometric, deuterium-labeled versions of the transition structure for the [1,3] carbon shift as defined geometrically through theoretical work by Quirante, Enríquez, and Hernando,^{94,95} and by Houk and co-workers⁹⁶:



This hypothetical model supposes that significant conformational changes of nonintermediate diradicals may precede transition states leading to cyclopentenenes. For the special case of deuterium-labeled vinylcyclopropane, it predicts that the ratio of *sr* to *ar* products should be equal to the ratio of *si* to *ai* products. Experimentally this appears to be the case within likely uncertainty: $sr : ar = (23 \pm 2) : (13 \pm 2) = 1.8 \pm 0.3$; and $si : ai = (40 \pm 2) : (24 \pm 2) = 1.7 \pm 0.2$.⁶⁷

Theory

The hypothetical picture sketched above falls far short of what is desired, for it is based on analogy and supposition rather than on a firm foundation of quantum-mechanical calculational results. Theoretical work on this problem has been slow to mature, for the species likely to be important to defining reaction paths are relatively large (13 atoms) open-shell diradicals. At high levels of theory, these complex systems and the vast domains of conformational space one might want to explore present daunting obstacles.

The earliest attempt to apply semiempirical theory to this rearrangement predicted that the "forbidden" *sr* path through a diradical transition state would be favored.⁹² The work demonstrated a commendable willingness to consider stereochemical options not sanctioned by Woodward-Hoffmann theory; however, the stereochemical prediction and the generalization that "antarafacial allylic rearrangements are not feasible in systems of this kind"⁹² proved to be in conflict with experimental fact.⁹³ More recent work has defined geometry and energy for a transition structure for the [1,3] shift using the AM1 method^{94,95} and at RHF/6-31G* and CASSCF/3-21G levels of *ab initio* theory.⁹⁶

Happily, two groups are now making real progress toward characterizing stationary points and defining reaction paths for the vinylcyclopropane-to-cyclopentene rearrangement using CASSCF(4,4)/6-31G* and density functional theory methods. The results to date secured by Houk and coworkers,^{97,98} and by Davidson and Gajewski,⁹⁹ are, generally speaking, in fair agreement. Both groups have located a diradical transition structure for the [1,3] shift and another corresponding to the "edge-to-face" diradical; the calculations of Houk and coworkers have also found one corresponding to the planar "edge-to-edge" diradical. All three transition structures are very close to one another in energy.

The hypothetical model sketched above is not identical in all respects with the map of reaction paths currently advanced by the theoreticians,^{98,99} and their findings and views may well prove a better approximation to the true mechanism. Time—and carefully designed experiments and further calculational efforts—should resolve the several differences which remain. But, already, the best theory available suggests that no reactive interme-

diates intervene and that, thanks to the conformational flexibility of the diradicals involved, one starting material may follow four stereochemically distinct paths to form cyclopentene products.^{98,99}

Conclusion

The general view of the mechanism of the vinylcyclopropane-to-cyclopentene rearrangement suggested here, one supported in part by the best theoretical efforts to date,^{98,99} brings to mind the insights offered by Salem and coworkers quoted previously,³⁰ and the more comprehensive understanding offered by Doering and Sachdev⁵⁸:

Whereas it has been adequate to consider *the* mechanism, or *the* transition state, for a reaction, as molecules become more complicated than hydrogen, the bond-breaking process may need to be viewed as a family of individual processes, the number of which increases with the complexity of the empirical formula and decreases in response to certain symmetry elements in the molecule. In general, the mechanism of the reaction then consists of the sum of many individual paths each of which contributes in proportion to its critical energy and entropy.

With the vinylcyclopropane to cyclopentene rearrangement and some few other thermal reactions studied in fair detail,¹⁰⁰ this consideration of a mechanism being a family of individual processes seems apt, even necessary. More specifically, reactions proceeding by way of diradical structures may involve "a vibrational manifold of states."⁵⁸ There will surely be other instances in which such conceptualizations of reaction mechanisms and of the nature of diradicals will be prompted by experimental findings or by theory in the future.

Acknowledgments

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References

1. N. P. Neureiter, *J. Org. Chem.*, **24**, 2044–2046 (1959).
2. E. Vogel, *Angew. Chem.*, **72**, 4–26 (1960), note 162; E. Vogel, R. Palm, K. H. Ott, unpublished.
3. C. G. Overberger and A. E. Borchert, *J. Am. Chem. Soc.*, **82**, 1007–1008, 4896–4899 (1960).
4. N. J. Demjanow and M. Dojarenko [*Ber. Dtsch. Chem. Ges.*, **55**, 2718–2727 (1922)] may have formed some cyclopentene inadvertently as they converted 1-(cyclopropyl)ethyltrimethylammonium hydroxide to vinylcyclopropane, but the experimental details included in their paper provide no basis for an informed judgment on this possibility.
5. M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 3547–3548 (1961).
6. C. A. Wellington, *J. Phys. Chem.*, **66**, 1671–1674 (1962).
7. W. von E. Doering and W. R. Roth, *Angew. Chem., Int. Ed. Engl.*, **2**, 115–122 (1963).
8. W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715–737 (1963).
9. S. W. Benson, A. N. Bose, and P. Nangia, *J. Am. Chem. Soc.*, **85**, 1388–1389 (1963).
10. K. W. Egger, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 5420–5424 (1964).
11. For a more recent experimental determination of the resonance energy of the allyl radical, see W. Tsang and J. A. Walker, *J. Phys. Chem.*, **96**, 8378 (1992).
12. H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866–1887 (1968).
13. H. M. Frey, *Adv. Phys. Org. Chem.*, **4**, 147 (1966).
14. S. Sarel, J. Yovell, and H. Sarel-Imber, *Angew. Chem., Int. Ed. Engl.*, **7**, 577 (1968).
15. C. D. Gutsche and D. Redmore, *Carbocyclic Ring Expansion Reactions*, Academic Press, New York, 1968, pp. 163–170.
16. H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969).
17. M. R. Willcott, R. L. Cargill, and A. B. Sears, *Prog. Phys. Org. Chem.*, **9**, 25 (1972).
18. J. J. Gajewski, *Hydrocarbon Thermal Isomerizations*, Academic Press, New York, 1980, pp. 81–87.
19. T. Hudlicky, T. M. Kutchan, and S. M. Naqvi, *Org. React.*, **33**, 247 (1985).
20. Z. Goldschmidt and B. Crammer, *Chem. Soc. Rev.*, **17**, 229 (1988).
21. (a) T. Hudlicky and J. W. Reed, In *Comprehensive Organic Synthesis*, Vol. 5, B. M. Trost, I. Fleming, and L. A. Paquette, Eds., Pergamon Press, Oxford, 1991, pp. 899–970; (b) T. Hudlicky, D. A. Becker, and R. L. Fan, updated by S. Kozhushkov, In *Houben-Weyl: Methods of Organic Chemistry*, Vol. E17, *Carbocyclic Three- and Four-Membered Ring Compounds*, A. de Meijere, Ed., Thieme, Stuttgart, 1996, pp. 2538–2565.
22. E. J. Corey and X.-M. Cheng, *The Logic of Chemical Synthesis*, John Wiley & Sons, New York, 1989, pp. 88–89.
23. B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958).
24. (a) W. L. Carter and R. G. Bergman, *J. Am. Chem. Soc.*, **90**, 7344 (1968); (b) R. G. Bergman, *J. Am. Chem. Soc.*, **91**, 7405 (1969); (c) R. G. Bergman and W. L. Carter, *J. Am. Chem. Soc.*, **91**, 7411 (1969).
25. J. E. Baldwin and C. B. Selden, *J. Am. Chem. Soc.*, **115**, 2239 (1993).
26. R. Hoffmann, *Tetrahed. Lett.*, 3819 (1965).
27. (a) R. Hoffmann, Abstracts of Papers, 151st American Chemical Society National Meeting, Pittsburgh, PA, March 1966; Paper 109 K; (b) R. Hoffmann, *Trans. NY Acad. Sci.*, 475–479 (1966); (c) R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 1475 (1968).
28. L. Salem, In *Reaction Transition States*, 21st Annual Meeting of the Société de Chimie Physique, J.-E. Dubois, Ed., Gordon and Breach, New York, 1972, pp. 97–108.
29. Y. Jean, L. Salem, J. S. Wright, J. A. Horsley, C. Moser, and R. M. Stevens, *Pure Appl. Chem.*, **1** (Suppl.), 197 (1971).
30. J. A. Horsley, Y. Jean, C. Moser, L. Salem, R. M. Stevens, and J. S. Wright, *J. Am. Chem. Soc.*, **94**, 279 (1972).
31. P. J. Hay, W. J. Hunt, and W. A. Goddard, *J. Am. Chem. Soc.*, **94**, 638 (1972).
32. S. N. Ragunathan, T. B. Freedman, L. A. Nafie, D. K. Lewis, D. A. Glenar, and J. E. Baldwin, *J. Am. Chem. Soc.*, **113**, 1864 (1991).
33. T. B. Freedman, S. J. Cianciosi, S. N. Ragunathan, J. E. Baldwin, and L. A. Nafie, *J. Am. Chem. Soc.*, **113**, 8298 (1991).
34. J. E. Baldwin and S. J. Cianciosi, *J. Am. Chem. Soc.*, **114**, 9401 (1992).
35. J. E. Baldwin, S. J. Cianciosi, D. A. Glenar, G. J. Hoffman, I.-W. Wu, and D. K. Lewis, *J. Am. Chem. Soc.*, **114**, 9408 (1992).
36. Y. Yamaguchi, H. F. Schaefer, and J. E. Baldwin, *Chem. Phys. Lett.*, **185**, 143 (1991).
37. J. E. Baldwin, Y. Yamaguchi, and H. F. Schaefer, *J. Phys. Chem.*, **98**, 7513 (1994).
38. S. J. Getty, E. R. Davidson, and W. T. Borden, *J. Am. Chem. Soc.*, **114**, 2085 (1992).
39. S. J. Getty, D. A. Hrovat, J. D. Xu, S. A. Barker, and W. T. Borden, *J. Chem. Soc. Faraday Trans.*, **90**, 1689 (1994).
40. J. E. Baldwin, In *The Chemistry of the Cyclopropyl Group*, Vol. 2, Z. Rapoport, Ed., John Wiley & Sons, Chichester, UK, 1995, pp. 469–494.
41. C. Doubleday, *J. Phys. Chem.*, **100**, 3520 (1996).
42. C. Doubleday, K. Bolton, G. H. Peslherbe, and W. L. Hase, *J. Am. Chem. Soc.*, **118**, 9922 (1996).
43. (a) A. H. Zewail, Lecture, 38th Conference on Chemical Research, Robert A. Welch Foundation, Houston, TX, October 24, 1994, *Conference Proceedings*, Ch. 8, pp. 129–155; (b) S. Pedersen, J. L. Herek, and A. H. Zewail, *Science*, **266**, 1359 (1994); (c) A. H. Zewail, Lecture, 1995 Peter A. Leermakers Symposium, Wesleyan University, May 4, 1995.
44. J. E. Baldwin, T. B. Freedman, Y. Yamaguchi, and H. F. Schaefer, *J. Am. Chem. Soc.*, **118**, 10934 (1996).
45. C. Doubleday, K. Bolton, and W. L. Hase, *J. Am. Chem. Soc.*, **119**, 5251 (1997).
46. D. A. Hrovat, S. Fang, W. T. Borden, and B. K. Carpenter, *J. Am. Chem. Soc.*, **119**, 5253 (1997).

47. R. B. Woodward and R. Hoffmann, *Angew. Chem. Int. Ed. Engl.*, **8**, 781 (1969).
48. R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, Verlag Chemie, Weinheim, 1970, pp. 121–122.
49. M. R. Willcott and V. H. Cargle, *J. Am. Chem. Soc.*, **89**, 723 (1967).
50. M. R. Willcott and V. H. Cargle, *J. Am. Chem. Soc.*, **91**, 4310 (1969).
51. W. von E. Doering and J. B. Lambert, *Tetrahedron*, **19**, 1989 (1963).
52. W. von E. Doering and E. K. G. Schmidt, *Tetrahedron*, **27**, 2005 (1971).
53. R. A. Clark, *Tetrahed. Lett.*, 2279 (1971).
54. J. S. Swenton and A. Wexler, *J. Am. Chem. Soc.*, **93**, 3066 (1971).
55. R. S. Cooke and U. H. Andrews, *J. Am. Chem. Soc.*, **96**, 2974 (1974).
56. P. H. Mazzocchi and H. J. Tamburin, *J. Am. Chem. Soc.*, **92**, 7220 (1970).
57. P. H. Mazzocchi and H. J. Tamburin, *J. Am. Chem. Soc.*, **97**, 555 (1975).
58. W. von E. Doering and K. Sachdev, *J. Am. Chem. Soc.*, **96**, 1168 (1974).
59. W. von E. Doering and K. Sachdev, *J. Am. Chem. Soc.*, **97**, 5512 (1975).
60. G. D. Andrews and J. E. Baldwin, *J. Am. Chem. Soc.*, **98**, 6705 (1976).
61. E. A. Barsa, *The Thermal Rearrangements of Substituted Cyclopropanes and the Stereochemistry of the Vinylcyclopropane Rearrangement*, Ph.D. Dissertation, Harvard University, 1977.
62. J. J. Gajewski and J. M. Warner, *J. Am. Chem. Soc.*, **106**, 802 (1984).
63. R. H. Newman-Evans, R. J. Simon, and B. K. Carpenter, *J. Org. Chem.*, **55**, 695 (1990).
64. J. E. Baldwin and N. D. Ghatlia, *J. Am. Chem. Soc.*, **113**, 6273 (1991).
65. J. E. Baldwin and S. J. Bonacorsi, *J. Am. Chem. Soc.*, **115**, 10621 (1993).
66. J. E. Baldwin and S. J. Bonacorsi, *J. Am. Chem. Soc.*, **59**, 7401 (1994).
67. J. E. Baldwin, K. A. Villarica, D. I. Freedberg, and F. A. L. Anet, *J. Am. Chem. Soc.*, **116**, 10845 (1994).
68. J. E. Baldwin and K. A. Villarica, *J. Org. Chem.*, **60**, 186 (1995).
69. L. A. Asuncion and J. E. Baldwin, *J. Org. Chem.*, **60**, 5778 (1995).
70. L. A. Asuncion and J. E. Baldwin, *J. Am. Chem. Soc.*, **117**, 10672 (1995).
71. J. E. Baldwin and S. J. Bonacorsi, *J. Am. Chem. Soc.*, **118**, 8258 (1996).
72. J. J. Gajewski and M. P. Squicciarini, *J. Am. Chem. Soc.*, **111**, 6717 (1989).
73. J. J. Gajewski and L. P. Olson, *J. Am. Chem. Soc.*, **113**, 7432 (1991).
74. J. J. Gajewski, L. P. Olson, and M. R. Willcott, *J. Am. Chem. Soc.*, **118**, 299 (1996).
75. D. G. Retzlöff, B. M. Coull, and J. Coull, *J. Phys. Chem.*, **74**, 2455 (1970).
76. D. K. Lewis, J. E. Baldwin, and S. J. Cianciosi, *J. Phys. Chem.*, **94**, 7464 (1990).
77. D. K. Lewis, D. J. Charney, B. L. Kalra, A.-M. Plate, M. H. Woodard, S. J. Cianciosi, and J. E. Baldwin, *J. Phys. Chem. A*, **101**, 4097 (1997).
78. For references to the original kinetic work providing data for Figure 1, and for further discussion of the radical stabilization values used, see ref. 40 and J. E. Baldwin, *J. Chem. Soc. Chem. Commun.*, 31 (1988).
79. J. S. Chickos, Abstracts of Papers, 187th American Chemical Society National Meeting, St. Louis, MO, April, 1984, ORGN 228. See also R. J. Crawford and D. M. Cameron, *Can. J. Chem.*, **45**, 691 (1967).
80. J. E. Baldwin and K. A. Villarica, *Tetrahed. Lett.*, **35**, 7905 (1994).
81. A. de Meijere and W. Lüttke, *Tetrahedron*, **25**, 2047 (1969).
82. M. Traetteberg, P. Bakken, A. Almenningen, and W. Lüttke, *J. Mol. Str.*, **189**, 357 (1988).
83. Microwave spectroscopic studies of vinylcyclopropane have provided structural information for the trans conformer: Z. Kisiel, P. W. Fowler, A. C. Legon, and P. Dixon, *J. Chem. Soc., Faraday Trans.*, **92**, 907 (1996).
84. G. R. De Maré and M. R. Peterson, *J. Mol. Struct. (Theochem)*, **6**, 213 (1982).
85. B. Klahn and V. Dyczmons, *J. Mol. Struct. (Theochem)*, **23**, 75 (1985).
86. B. K. Carpenter, *Acc. Chem. Res.*, **25**, 520 (1992).
87. B. K. Carpenter, *J. Org. Chem.*, **57**, 4645 (1992).
88. J. E. Baldwin and K. Belfield, *J. Am. Chem. Soc.*, **110**, 296 (1988).
89. F.-G. Klärner, R. Drewes, and D. Hasselmann, *J. Am. Chem. Soc.*, **110**, 297 (1988).
90. J. E. Baldwin and K. D. Belfield, *J. Phys. Org. Chem.*, **2**, 455 (1989).
91. B. K. Carpenter, *J. Am. Chem. Soc.*, **118**, 10329 (1996).
92. M. J. S. Dewar, G. J. Fonken, S. Kirschner, and D. E. Mitner, *J. Am. Chem. Soc.*, **97**, 6750 (1975).
93. G. D. Andrews and J. E. Baldwin, *J. Am. Chem. Soc.*, **98**, 6706 (1976).
94. J. J. Quirante, R. Enríquez, and J. M. Hernando, *J. Mol. Struct. (Theochem)*, **204**, 193 (1990).
95. J. J. Quirante, R. Enríquez, and J. M. Hernando, *J. Mol. Struct. (Theochem)*, **254**, 493 (1992).
96. K. N. Houk, Y. Li, and J. D. Evanseck, *Angew. Chem. Int. Ed. Engl.*, **31**, 682 (1992); see also K. N. Houk, *Acc. Chem. Res.*, **28**, 81 (1995).
97. O. Wiest, J. Storer, J. Fennen, M. Nendel, and K. N. Houk, Abstracts of Papers, 210th American Chemical Society National Meeting, Chicago, IL, August 1995, ORGN 33.
98. K. N. Houk, M. Nendel, O. Wiest, and J. W. Storer, *J. Am. Chem. Soc.*, **119**, 10545 (1997).
99. E. R. Davidson and J. J. Gajewski, *J. Am. Chem. Soc.*, **119**, 10543 (1997).
100. (a) D. K. Lewis, B. Brandt, L. Crockford, D. A. Glenar, G. Rauscher, J. Rodriquez, and J. E. Baldwin, *J. Am. Chem. Soc.*, **115**, 10621 (1993); (b) D. K. Lewis, A. Hutchinson, S. J. Lever, E. L. Spaulding, S. J. Bonacorsi, and J. E. Baldwin, *Israel J. Chem.*, **36**, 233 (1996).